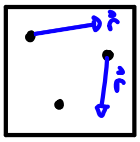
3-12-20

Thermodynamics + Microscopic Physics



Gas particles have mass m : Describe "Microscopic" states of System

→ Use microscopic states to generate entropy $S = S(E, V, N)$

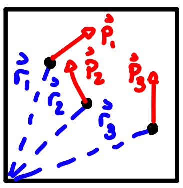
→ Generate equations of state via

→ $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}$, $\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}$

→ Thermodynamic relations

Non-interacting gas : microstates, macrostates

- gas N non-interacting particles



describe State by listing all positions + momenta

Particle	Position	Momentum
1	$\vec{r}_1$	$\vec{p}_1$
2	$\vec{r}_2$	$\vec{p}_2$
3	$\vec{r}_3$	$\vec{p}_3$
⋮	⋮	⋮
N	$\vec{r}_N$	$\vec{p}_N$

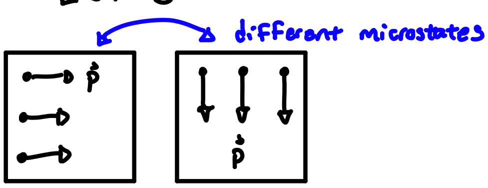
Single state of gas $S = \{\vec{r}_1, \vec{p}_1, \vec{r}_2, \vec{p}_2, \dots\}$

For any microstate Can Compute :

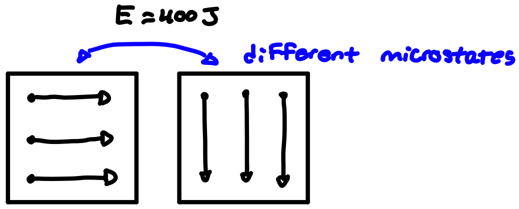
1) Number of particles N (count)
2) Volume V (geometry / configuration)
3) Energy $E = \sum_{\text{all } i} \frac{\vec{p}_i^{\,2}}{2m}$ (from microstate)

There are many microstates for the system. For many microstates the bulk parameters can be the same

E = 100 J



E = 400 J



Same E, V, N each.
These two microstates
represent same macrostate

Same E, V, N
Different macrostate

Macrostate - State defined by bulk properties
- Can be represented by many different microstates

Describe macrostates $\longrightarrow$ List possible <u>microstates</u> that represent macrostate $s_1, s_2, s_3 \dots$

↳ Provide a rule that gives probability with which each microstate occurs: $p(s_1), p(s_2), \dots$

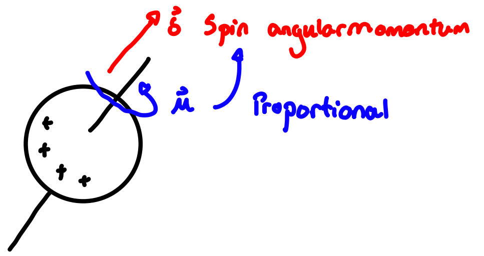
↳ Use these to generate entropy

$S = S(E, V, N)$

↳ Probs

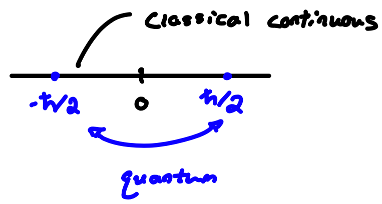
Spin - ½ Systems

Non-interacting Spin-½ particles. A Spin-½ particle is one whose magnetic dipole moment $\vec{\mu}$ obeys particular rules

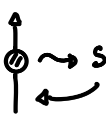


Spin-½ particle ~ Quantum theory
~ Nuclei, Subatomic particles

Key rules:
1) If one measures one component of spin there are two possible outcomes
2) There are states that yield either with certainty



Spin up



$S_z = +\hbar/2$ certainty

dipole moment component

$\mu_z = +\mu$

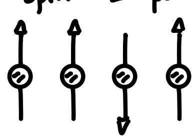
Spin down

$S_z = -\hbar/2$ certainty

dipole moment component

$\mu_z = -\mu$

Multiple Spin-½ particles



$M = +2\mu$

Magnetization:

$$M = \sum_{\text{all particles}} \mu_z$$

Dipole in an external field $\vec{B}$ potential energy is

$$U = -\vec{\mu} \cdot \vec{B}$$

Suppose $\vec{B}$ is along $\hat{z}$. For single particle

$$U = -\mu_z B$$

For entire collection

$$E = -\mu B$$

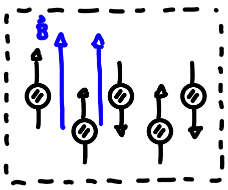
System of these:

1) There are N spin-½ particles
2) They do not interact with each other
3) Any single particle there are two states
   up ↑ down ↓

Macrostate will be specified via

1) N = number of particles
2) M = magnetization
3) E = energy $E = -BM$

Microstate ~ spin for each particle



N particles

→ Determine M

→ Determine energy $= -BM$

→ Entropy : $S = (E, M, N)$

Microstates and Macrostates for Spin-½ Systems

magnetization can be determined using:

N_+ = number spin up

N_- = ... spin down

$$\Rightarrow M = \mu N_+ + (-\mu) N_-$$

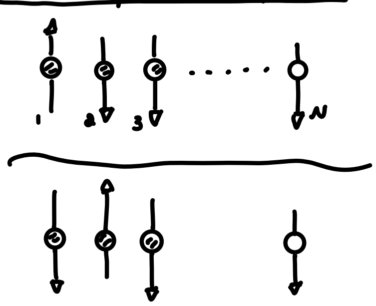
$$M = \mu (N_+ - N_-)$$

Macroscopic description

Provide N_+, N_-

e.g. $N_+ = 1$, $N_- = N-1$

Microscopic description



Many microstates represent same macrostates

Will need probabilities with which microstates occur → give probabilities for macrostates

Depends on situation:

1) restricted case $B = 0$

   For a single particle $\text{Prob}(\uparrow) = ½$

   $\text{Prob}(\downarrow) = ½$

2) general ($B \neq 0$)

$$\text{Prob}(\uparrow) = \frac{1+\varepsilon}{2}$$

$$\text{Prob}(\downarrow) = \frac{1-\varepsilon}{2} \qquad \varepsilon \text{ depend on } B, T, \ldots$$

If there is no external field then all microstates are equally likely

Probability with which any macrostate occurs depends on number of microstates that represent macrostate

Multiplicity of macrostate

Ω = number of microstates that represent macrostates

e.g. system of N spin-$\frac{1}{2}$ particles :

$$\Omega(N_+) = \binom{N}{N_+}$$

If $B=0$ then

$$\text{Prob(Macrostate)} = \frac{\Omega(N_+)}{\text{total number of microstates}}$$

General ($B \neq 0$) : if $p = \text{prob}(\uparrow)$ and $q = \text{prob}(\downarrow)$ then

$$\text{Prob(Macrostate } N_+) = \Omega(N_+)\, p^{N_+} q^{N-N_+} = \binom{N}{N_+} p^{N_+} q^{N-N_+}$$

3-31-20

Statistical description of thermal systems

Collection of N spin-$\frac{1}{2}$ particles macroscopic state (bulk)
~ number with spin up, N_+

Microscop states (system details) ~ arrangement of spins for individual particles

$\downarrow$

List possible macrostates : $N_+ = 0, 1, 2, \ldots, N$

$\downarrow$

For each macrostate, list microstates

e.g.

$N_+ = 1 \quad \uparrow \downarrow \downarrow \ldots \downarrow \downarrow \longrightarrow$ Provide single particle probabilities

$\text{Prob}(\uparrow) = p$

$\text{Prob}(\downarrow) = q = 1-p$

$\downarrow$

Probabilities for macrostates

$$\text{prob}(N_+) = \binom{N}{N_+} p^{N_+} q^{N-N_+}$$

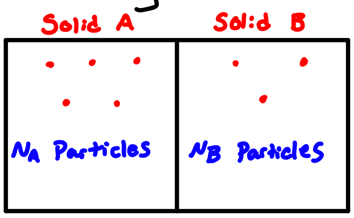
Multiplicity of a microstate, Ω, is number of microstates that represent macrostate.

For spin-$\frac{1}{2}$ particles :

$$\Omega(N_+) = \binom{N}{N_+} = \frac{N!}{N_+!\,(N-N_+)!}$$

Einstein Solids

- Collection of quantum harmonic oscillators
- Oscillators are all identical, but distinguishable
- interacting Einstein Solids



Energy E_A Energy E_B

- which way does energy flow?
- energy per particle in equilibrium

$$\frac{E_A}{N_A} \quad vs. \quad \frac{E_B}{N_B}$$

Quantum oscillator basics:

1) Each oscillator has angular frequency. ω
2) Energies available are:

$$\frac{1}{2}\hbar\omega, \ \frac{3}{2}\hbar\omega, \ \frac{5}{2}\hbar\omega, \ \ldots$$

in general

$$E_n = \hbar\omega(n + 1/2) \qquad n = 0, 1, 2, 3, \ldots$$

3) Can label state of a single oscillator using "n"

N oscillators

$\odot^1 \quad \odot^2 \quad \ldots \quad \odot^N$

State $\quad n_{(1)} \quad n_{(2)} \quad n_{(N)}$

Energy $\hbar\omega(n_{(1)} + 1/2)$

Macrostate ~ described by total energy of system total energy

$$E = \underbrace{E_{(1)}}_{\text{Energy of oscillator } 1} + E_{(2)} + \ldots + E_{(N)}$$

$$= \hbar\omega[n_{(1)} + 1/2] + \hbar\omega[n_{(2)} + 1/2] + \ldots$$

$$= \hbar\omega[n_{(1)} + n_{(2)} + \ldots + n_{(N)}] + \hbar\omega\frac{N}{2}$$

Energy units:

$$q = n_{(1)} + n_{(2)} + \ldots + n_{(N)}$$

energy is $E = \hbar\omega(q + N/2)$

macrostate $\rightarrow$ (describe q, N)

Interacting Einstein Solids

Solid A	Solid B
Particles N_A	Particles N_B
Macrostate q_A	Macrostate q_B

Energy E_A Energy E_B

$$E_A = \hbar\omega(q_A + N_A/2)$$
$$E_B = \hbar\omega(q_B + N_B/2)$$

Total energy $E = \hbar\omega\left(q_A + q_B + \frac{N_A + N_B}{2}\right)$

$\rightarrow$ assume that N_A, N_B fixed E, fixed

Total energy units $\underset{\text{Fixed}}{q} = \underset{\text{vary}}{q_A + q_B}$

Macrostate described by N_A, N_B, q_A, q_B. Assume systems can exchange energy. Also each microstate for entire system is equally likely

$$\text{Prob}(N_A, N_B, q_A, q_B) = \frac{\Omega(N_A, N_B, q_A, q_B)}{\#\text{ of microstates}}$$

and

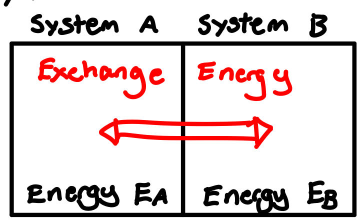
$$\Omega(N_A, N_B, q_A, q_B) = \Omega_A(N_A, q_A)\,\Omega_B(N_B, \underbrace{q_B}_{q - q_A})$$

4-2-20

Equilibrium States + Statistics

Interacting systems

Isolated from environment



- Total number of particles N is fixed
- Total energy E, is fixed
- N_A = Number of particles in A
  N_B = " " in B
  E_A = Energy of A
  E_B = " " B

Macrostate of A $\rightsquigarrow$ Specify N_A, E_A
Macrostate " " " N_B, E_B

Comined System
Macrostate of combo $\rightsquigarrow$ N_A, N_B, E_A, E_B
Constraints: $E = E_A + E_B$ is fixed
N_A fixed
N_B fixed

Describe Macrostate:
Fixed: E, N_A, N_B $\longrightarrow$ Macrostate given by E_A, E_B so that $E = E_A + E_B$ is fixed

For any macrostate many possible microstates
Assumption: For an isolated system with energy, E, the probabilities with which any microstate (same energy E) occurs are all the same.

Multiplicity of microstates for entire system:
$\Omega(N, E)$ = number of microstates for combined system N particles (N_A in A, N_B in B) and energy E.

For pair of systems:
$\underbrace{\Omega(N_A, N_B, E_A, E_B)}_{\text{Macrostate}}$ = multiplicity of macrostate
= number of microstates that represent this macrostate

$$\Omega(N_A, N_B, E_A, E_B) = \Omega_A(\underbrace{N_A, E_A}_{M_A})\,\Omega_B(\underbrace{N_B, E_B}_{M_B})$$

$$\text{Prob}(N_A, N_B, E_A, E_B) = \frac{\Omega_A(N_A, E_A)\,\Omega_B(N_B, E_B)}{\Omega(N,E)}$$

$\leftarrow$ # of microstates for this macrostate

$\leftarrow$ Total # of microstates for all possible macrostates

$N = N_A + N_B$, $E = E_A + E_B$

Example : Suppose $E = 1000\,J$

	E_A	E_B	Ω_A	Ω_B	Ω
	100 J	900 J	1	10	10
one macrostate $\longrightarrow$	200 J	800 J	3	9	27
" " $\longrightarrow$	300 J	700 J	6	8	48
.....	400 J	600 J	10	7	70

<u>Assumption :</u> For a system with many possible macrostates the equilibrium state is the most probable state.

Technical Issue : Find $\Omega(N, E)$

e.g. Einstein Solid $E = \hbar\omega(q + N/2)$

$\hookrightarrow$ Total number of energy units 0, 1, 2, 3, ...

Macrostate N, E $\longrightarrow$ describe via N and $q = \frac{E}{\hbar\omega} - \frac{N}{2}$ — Multiplicity $\Omega = \binom{N+q-1}{q}$

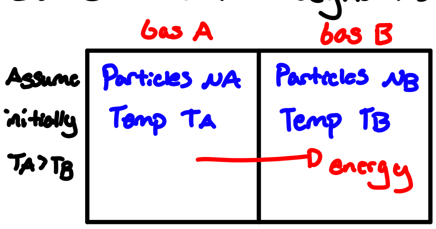
Interacting Einstein Solids Found :

1) most probable macrostate (i.e. equilibrium state) is that for which energy per particle approximately equal

$$\frac{E_A}{N_A} \approx \frac{E_B}{N_B}$$

2) Energy flows from system with higher E/N to system with lower E/N.

Connect to thermodynamics? Monoatomic ideal gases.



$\longrightarrow$ $E_A = \frac{3}{2} N_A k T_A$, $\frac{E_A}{N_A} = \frac{3}{2} k T_A$, $\frac{E_B}{N_B} = \frac{3}{2} k T_B$

Second law says that energy flows from higher to lower temp. $\longleftrightarrow$ Statistical analysis said energy flows from higher to lower energy.

<u>Entropy and Statistics</u>

Postulate : Energy of system (analyzed with micro/macrostates) is

$$S(E,N) = k \ln[\Omega(E,N)]$$

where $\Omega(E,N)$ is multiplicity of macrostate with energy E, N

Need to show :

1) requirements for entropy
   - is additive
   - gives correct equilibrium state
2) Matches entropies for various thermodynamic systems :
   - ideal gas
   - oscillating solids

This definition gives :

For an isolated system consisting of subsystem A, B, C, ...

$$S = S_A + S_B + S_C + \ldots\ldots$$

Total System   Entropy of A

For an isolated system, statistical requirement for equilibrium state (most probable) $\longrightarrow$ state for which entropy is a max

because $S = k\ln[\Omega]$

largest for most probable

When subsystems A, B, C, ... interact, the equilibrium state when

$$\frac{\partial S_A}{\partial E_A} = \frac{\partial S_B}{\partial E_B} = \frac{\partial S_C}{\partial E_C} \ldots \Rightarrow T_A = T_B = T_C$$

Scheme : (Stat Phys)

Statistical model $\longrightarrow$ Entropy $S(E,N) = k\ln[\Omega(E,N)]$

~ describe micro/macrostates

~ determine multiplicities $\Omega(E,N)$

Entropy : * adds

* max for equilibrium states

Postulates: * For an isolated system energy E all microstates are equally possible

* Equilibrium State = most probable macrostate.

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_N$$

Multiplicities

e.g. Einstein Solid

$$\Omega(N,q) = \binom{N+q-1}{q} = \frac{(N+q-1)!}{q!(N-1)!}$$

when N, q are large?

Stirlings approximation

If N is sufficiently large then : $N! \approx N^N e^{-N}\sqrt{2\pi N}$

and

$$\ln(N!) = \ln(N^N e^{-N}\sqrt{2\pi N})$$

$$= \ln(N^N) + \ln(e^{-N}) + \ln(\sqrt{2\pi N})$$

$$\ln(N!) = N\ln(N) - N + \frac{1}{2}\ln(2\pi N)$$

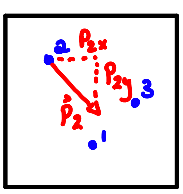
4-7-20

Statistical physics for particles with position + momentum

Gas consisting of :

1) N distinguishable molecules each mass m.

2) molecules do not interact with each other



3) Region that they can occupy has volume V
4) Energy of Ensemble, E

$\boxed{\text{Macrostate} \rightsquigarrow \text{Specify } E, V, N}$

Microstate $\rightsquigarrow$ position and momentum of each molecule

Particle	Position	Momentum
1	x_1, y_1, z_1	p_{1x}, p_{1y}, p_{1z}
2	x_2, y_2, z_2	p_{2x}, p_{2y}, p_{2z}
3	$\vdots$	$\vdots$
$\vdots$		

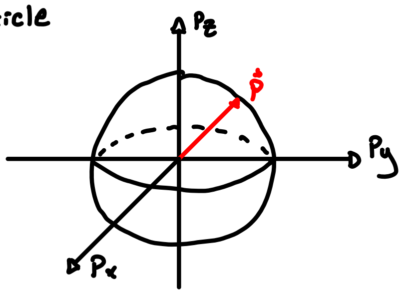
Connection to macrostate via total Energy

$$E = \frac{\vec{p}_1^{\,2}}{2m} + \frac{\vec{p}_2^{\,2}}{2m} + \dots = \frac{1}{2m}\left\{ p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + p_{2x}^2 + p_{2y}^2 + p_{2z}^2 + \dots \right\}$$

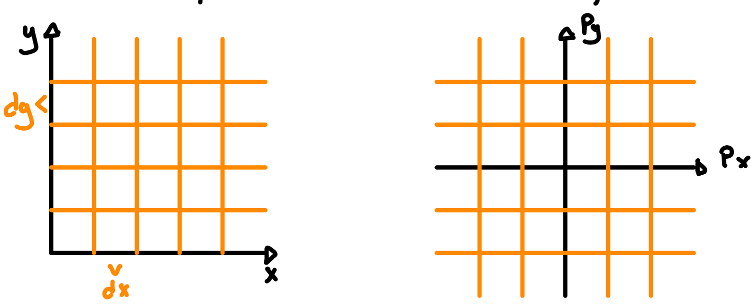
Multiplicity $\Omega(E,V,N) \rightsquigarrow S(E,V,N) = k \ln[\Omega(E,V,N)]$
$\hookrightarrow \infty$??

Single Particle

$$E = \frac{\vec{p}^{\,2}}{2m}$$



To avoid this problem could discretize space of states



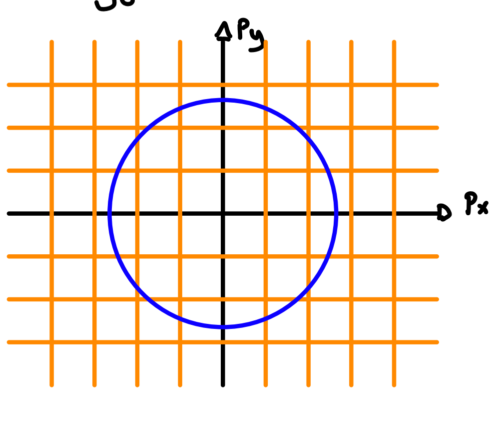
$\rightsquigarrow$ one cell from each diagram is one state for one particle

Note that energy only depends on momentum. Need to count states by counting cells
- Position (same regardless of energy)
- Momentum (only count cells that give correct energy)

Single particle in two dimensions

$$E = \frac{1}{2m}(p_x^2 + p_y^2)$$

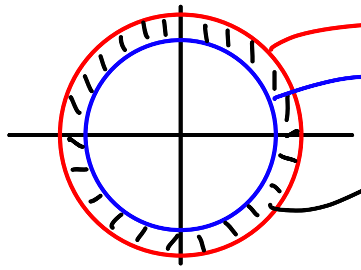
For a given energy how do we locate states cells with this energy?



$p_x^2 + p_y^2 = 2mE \rightsquigarrow$ circle radius $\rightsquigarrow \sqrt{2mE}$
Count cells on circle radius $\sqrt{2mE}$

Density of States

Want to count number of states with energy $E \to E + dE$.
Eventually take limit as $dE \to 0$
Rather, count total number of states in $0 \to E$.



$$\boxed{\Gamma(E) = \text{Total number of microstates with energy } 0 \to E}$$

Number of states in range $E \to E + dE$ $\quad \Gamma(E+dE) - \Gamma(E) \approx \Omega(E)$

For $dE \to 0$

$$\Gamma(E+dE) - \Gamma(E) = \frac{d\Gamma}{dE}\, dE \approx \Omega(E)$$

Density of states :

$$g(E) = \frac{d\Gamma}{dE}$$

Number of states in range

$$\boxed{E \to E + dE = g(E)\, dE \approx \Omega(E)}$$

Entropy $\quad \boxed{S(E,V,N) = k \ln\left[g(E,V,N)\, dE\right]}$

Calculating density of states

How to get Γ, g ?

Gas of quantum particles

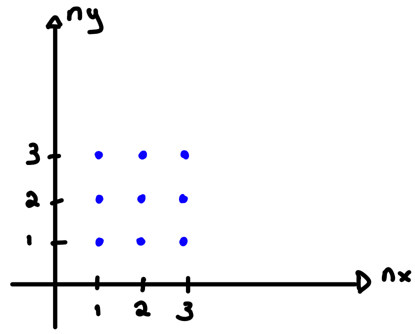
N distinguishable quantum particles in infinite well - cubic - dimensions $L \times L \times L$

Quantum theory : (single particle)

1) State of particle represented by 3 integers
$\quad n_x, n_y, n_z = 1, 2, 3, 4 \ldots$
2) Energy is
$$E = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

Example of particle states + energies

State			Energy
n_x	n_y	n_z	E
1	1	1	$3\, h^2/8mL^2$
1	1	2	$4\,\dfrac{h^2}{8mL^2}$
1	2	1	
2	1	1	



Can represent states in a three dimensional n_x, n_y, n_z space
Illustrate two dimensions. States are represented by dots.
Can use geometry to get $\Gamma(E)$.

4-9-20

Gas of Quantum Particles

Single particle in an infinite cubic well

* States are labeled by n_x, n_y, n_z integers
* energy $E = \frac{h^2}{8mL^2}[n_x^2 + n_y^2 + n_z^2]$

Consider N non-interacting distinguishable particles

#1 #2 #3 #4

$n_{1x}\, n_{1y}\, n_{1z}$ " " " " " "

Energy

$$E = \frac{h^2}{8mL^2}\left[n_{1x}^2 + \dots\dots n_{3z}^2\right]$$

Need

$$\Gamma(E) = \#\text{ states with energy } 0 \to E$$

density of states :

$$g(E) = \frac{d\Gamma}{dE}$$

Entropy $S = k\ln[g(E)\,dE]$

Ensembles of Systems

Scheme for statistical physics :

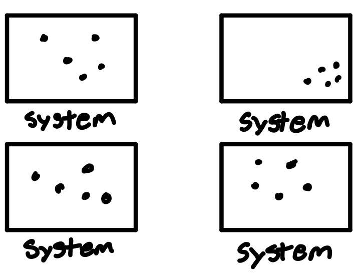
Macrostates : E, V, N ? $\longrightarrow$ Microstates - Multiplicity Ω $\longrightarrow$ Entropy $S = k\ln(\Omega)$

Alternative scheme :

Describe system and its states $\{s\}$ $\longrightarrow$ Rule for probability with which state occurs

Use probabilities to get entropy

Imagine ensembles of systems :



$\longrightarrow$ List possible states for any single ensemble member

$\downarrow$

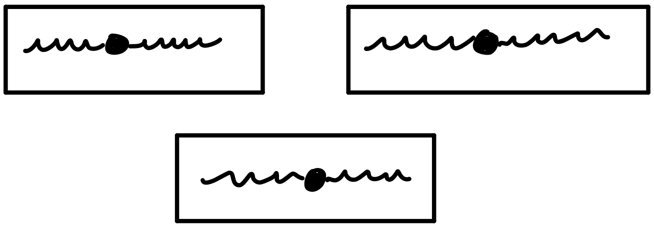
Probability with which the system occurs

$\downarrow$

Entropy from probabilities

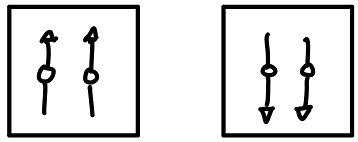
Systems can consist of few or many particles

1) Each system has one particle

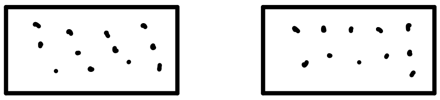


Systems consist of two particles

2) Each system has two particles



3) Many particles



Need to decide on meaning of "system" and then:

1) describe possible states of system
2) Energy of states

<u>Examples</u>: 1) one dim quantum oscillator

$\sim$ states labeled with $n = 0, 1, 2, \dots$

2) One dimensional well

$\sim$ states labeled with $n = 1, 2, 3, \dots$

3) Hydrogen atom: (n, ℓ, m_ℓ, m_s)

$n = 1, 2, 3, \dots$

$\ell = 0, 1, 2, \dots, n-1$

$m_\ell = -\ell, -\ell+1, \dots, \ell-1, \ell$

$m_s = +\frac{1}{2}, -\frac{1}{2}$

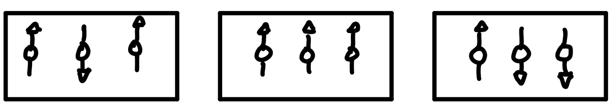
<u>Scheme</u>: Describe possible states via labels $\{s\}$

Let

P_s = probability that system is in state s

Can prove: The average entropy per system in an ensemble of these system is

$$S = -k \sum P_s \ln[P_s]$$

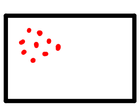


Multiplicity of supersystem in terms of states for individual systems (s)

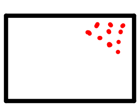
use $S = k \ln \Omega$

4-14-20

<u>States and Ensembles of Systems: General Framework</u>



System (Ensemble member)



System

For each ensemble member (system)

* list possible states for system $\sim$ label "s"
* determine probability with which state s occurs $\sim P_s$

Entropy of System

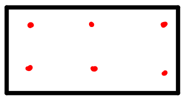
$S = -k \sum P_s \ln[P_s]$

Can assign values to measureable quantities, e.g. E (energy)
- need to use microscopic physics to determine value for each possible state, s $\rightsquigarrow$ e.g. energy need E_s

e.g. two molecules

Scheme

System State "s" $\longrightarrow$ Measureable quantity A need value for this state $\longrightarrow$ Mean value of A:



$$A_s$$

$$\bar{A} = \sum A_s P_s$$

For a thermodynamic ensemble of these systems value of A is $\bar{A}$

Need rules for getting probabilities.
- depends on general nature of system:

<u>Microcanonical Ensemble</u>

1) Every system has same fixed number of particles
2) Every system has same fixed energy - discrete energies : E
3) " " - Continuous engergies : $E \to E + dE$

<u>Discrete Energy Case - energy E</u>

- number of states is $\Omega(E)$
- assumption : all states with this energy equally likely

$$P_s = \frac{1}{\#\text{ of states}} \Rightarrow P_s = \frac{1}{\Omega(E)}$$

- entropy

$$S = -k \sum p_s \ln[p_s]$$
$$= -k \sum \frac{1}{\Omega} \ln\left[\frac{1}{\Omega}\right] = -k \frac{1}{\Omega} \ln\left[\frac{1}{\Omega}\right] \Sigma$$

$$S = -k \ln\left[\frac{1}{\Omega}\right] \Rightarrow S = k \ln[\Omega(E)]$$

<u>Canonical Ensemble</u>

- all systems have same fixed number of particles, N
- all particles are in thermal equilibrium with bath at temperature T
- need probabilities of system is in state s

Let s be any state of system, E_s be energy of state
Then probability in state s is

$$P_s = \frac{e^{-E_s/kT}}{Z}$$

where

$$Z = \sum e^{-E_s/kT}$$ (Partition Function)

Notation $\beta = \frac{1}{kT}$

$P_s = \frac{e^{-E_s\beta}}{Z}$ partition fn. $Z = \sum e^{-\beta E_s}$

Mean energy $\bar{E}$ represents energy E

$\bar{E} = \sum E_s P_s = \sum E_s e^{-E_s\beta}/Z$

$$\bar{E} = \frac{1}{Z}\sum_{\text{all } s} E_s e^{-E_s\beta}$$

$$= \frac{1}{Z}\sum_{\text{all } s} -\frac{\partial}{\partial\beta}\left(e^{-E_s\beta}\right) = -\frac{1}{Z}\frac{\partial}{\partial\beta}\sum_{\text{all } s} e^{-E_s/\beta} \quad : \quad \bar{E} = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = -\frac{\partial}{\partial\beta}(\ln Z)$$

$$\bar{E^2} = \frac{1}{Z}\frac{\partial^2 Z}{\partial\beta^2} \qquad \sigma_E^2 = -\frac{\partial\bar{E}}{\partial\beta}$$

4-16-20

Canonical Ensemble

System is in equilibrium with a resevoir at temperature T → system temperature is T

→ Describe system states ~ "s"

→ Microscopic physics gives energy of each state E_s

→ Partition Function $Z = \sum e^{-E_s\beta}$, $\beta = \frac{1}{kT}$ → Probability system is in state s is $p_s = e^{-E_s\beta}/Z$

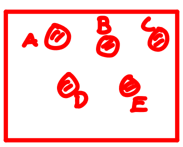
→ Mean energy $\bar{E} = -\frac{\partial}{\partial\beta}\ln(Z)$ → Entropy $S = k\ln(Z) + \frac{\bar{E}}{T}$ → Helmholtz free energy $F = -kT\ln(Z)$

Entropy and Helmholtz Free Energy

$$S = -k\sum p_s \ln[P_s] \Rightarrow S = k\ln[Z] + \bar{E}/T \Rightarrow F = -kT\ln(Z)$$

Multiple Particles

Canonical ensemble for a system with multiple particles



Z = partition function for entire system of all particles

Can one construct Z from :

Z_A = Partition Function for system only containing A.
Z_B = " " B.

Scheme : Given partition functions Z_A, Z_B, Z_C → Construct easily Z from Z_A, Z_B

If systems $A, B, C, D, \ldots$ are distinguishable and non-interacting then

$$Z = Z_A, Z_B, Z_C$$

where Z_A = partition function for system just containing A

Energy for multiple non-interacting distinguishable particles

Want $\bar{E}$ in terms $\bar{E}_A, \bar{E}_B, \bar{E}_C, \ldots$

$$\bar{E} = -\frac{\partial}{\partial\beta}\ln[Z] = -\frac{\partial}{\partial\beta}\ln[Z_A Z_B Z_C, \ldots] = \underbrace{-\frac{\partial}{\partial\beta}[\ln Z_A]}_{\bar{E}_A} \underbrace{- \frac{\partial}{\partial\beta}\ln[Z_B]}_{\bar{E}_B} \underbrace{- \frac{\partial}{\partial\beta}\ln[Z_C]}_{\bar{E}_C} \ldots$$

$\bar{E} = \bar{E}_A + \bar{E}_B + \bar{E}_C + \ldots$ energy is additive

Uncertainty ??

$$\sigma_E^2 = \sigma_{EA}^2 + \sigma_{EB}^2 + \ldots \longrightarrow \sigma_E = \sqrt{\sigma_{EA}^2 + \sigma_{EB}^2 + \ldots}$$

Thermodynamic Ensemble

- Consists of a large number of identical distinguishable system
- Then partition function for ensemble of N identical, distinguishable, non-interacting systems is

$$Z_{\text{ensemble}} = (Z_{\text{single particle}})^N$$

where

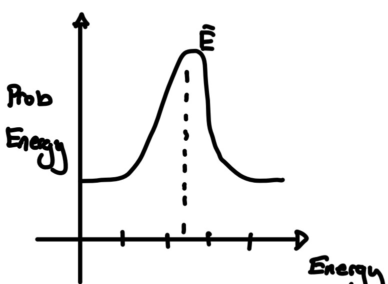
$$Z_{\text{single particle}} = \sum_i e^{-E_s\beta}$$

$$\bar{E}_{\text{ensemble}} = N\bar{E}_{\text{single particle}}$$

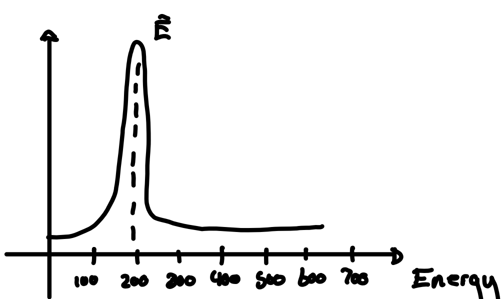
$$\sigma_{E\text{ ensemble}} = \sqrt{N}\,\sigma_{E\text{ single particle}}$$

Then statistical physics gives $\bar{E} \rightarrow$ Thermodynamics $E = \bar{E}$

What about fluctuations in $\bar{E}$



one particle



100 particles

As N increases $\bar{E}$ better represents possible energies. Can check via

$$\frac{\sigma_{E\,N\text{ particles}}}{\bar{E}_{N\text{ particles}}} = \frac{\sqrt{N}\,\sigma_{E\text{ one}}}{N\,\bar{E}_{\text{one}}} = \frac{1}{\sqrt{N}}\left(\frac{\sigma_{E\text{ one}}}{\bar{E}_{\text{one}}}\right) \longrightarrow 0 \text{ as } N \to \infty$$

4-21-20

Canonical Ensemble

Partition Function $Z = \sum e^{-E_s\beta}$

Then $\bar{E} = -\frac{\partial}{\partial\beta} \ln[Z]$

Ensemble of N distinguishable particles

Indistinguishable Particles

Suppose that states of single particle are:

State "s"	Energy E_s
0	0
1	ϵ
2	2ϵ
3	3ϵ
⋮	⋮

Distinguishable

A B C
0 0 0
0 0 ϵ

A B C
0 0 0
0 ϵ 0

Counts as two states in partition function

Indistinguishable

0 0 0
0 0 ϵ

0 0 0
0 ϵ 0

Only counted once in partition function

Scheme:

List all states of a single particle ~ $\{s\}$ and energies

↓

For N indistinguishable particles let
ν_s = number in state s

↓

State of ensemble is specified by $(\nu_0, \nu_1, \nu_2, \ldots)$ → constraint $\sum \nu_s = N$

↓

Energy of the ensemble state
$E(\nu_0, \nu_1, \nu_2, \ldots) = \sum \nu_s E_s$

↓

Partition Function
$$Z = \sum e^{-E(\nu_0, \nu_1, \ldots)\beta} = \sum e^{-\sum \nu_s E_s \beta}$$